Removal of Cadmium (II) from Aqueous Solution by using Leucaena Leucocephala Pods

Abdul Asyraf Ali Abdul Rahman, Noor Harliza Abd razak

Faculty of Chemical Engineering, Universiti Teknologi MARA (UiTM)

ABSTRACT

Heavy metals in wastewater is a growing concern whereby industrialization and populace growth were the major factors of many rising heavy metal ions in wastewater. One of the toxic heavy metal ions is Cd (II) ion where it was studied by the adsorption of Cd (II) on pods of Leucaena *Leucocephala* (LL). Sequestration of heavy metal ions by using adsorption technique utilizing bio adsorbent is developing as a economical potential option. Thermo Gravimetric Analysis (TGA), Fourier Transform Infrared (FTIR) Spectroscopy, Inductively Coupled Plasma (ICP), X-Ray Fluorescence (XRF) and Point Zero Charge were used to characterize the pods of Leucaena *Leucocephala* (LL). The effect of adsorbent dosage, pH and contact time were investigated through batch experiment in this study. The optimum removal of Cd (II) ion were found at concentration of 50 mg/L, pH 8, 0.25g of adsorbent dosage and a 160 min of contact time. This study revealed that the Leucaena *Leucocephala* pods are also a viable alternative as it is economical of bio adsorbent for Cd (II) ions removal in wastewater discharged from industry.

Keywords: Leucaena Leucocephala pods, Cd (II), Adsorption, Wastewater.

I. INTRODUCTION

Urbanization and populace growth have prompted the rise of many rising toxins, for example, heavy metals ions. The adsorption of lethal substances coming about because of the gathering of industrial wastes is vital and a standout amongst the most hazardous difficulties confronting the earth. These heavy metals ions contains metal particles that give a critical hazard to environment and human, in light of their high poisonous quality at both low and high concentration in soil and water [1]. Agricultural advancement on reasonable premise has prompted an ascent in the production of lignocellulosic biomass in Malaysia that offers tremendous potential to grow high esteem bio-based materials and items [2].

Cadmium is the most concerned harmful overwhelming metal that has brought about soil and water contamination because of its high versatility and perseverance [3]. The introduction of cadmium into nature has been expanding significantly which is basically ascribed to the mining and refining of cadmium minerals regularly related metallurgical businesses. A few industrial products that are in charge of the raising cadmium proportion in the earth because of metal plating, cadmium-nickel batteries, shades, pottery, photo, material printing materials [4]. The extraction of cadmium ions from polluted water is imperative profit by both financial and ecological because of its high poisonous quality to creatures, plants and humans [5].

Table 1: Various agricultural adsorbents used for removal of cadmium.

ADSORBENT	REFERENCE
Auricularia Auricular	[6]
Banana Peel	[7]
Carica Papaya	[8]
Citrus	[9]
Dicerocaryum Eriocarpum	[10]
Grapefruit	[11]
Lentil Husk	[12]
Morus Alba	[13]
Pleurotus Ostreatus	[14]
Rice Straw	[15]
S. Filipendula	[16]
Solidago Canadensis	[17]
Sorrel and Rocket Plant	[18]
Sweet Potato	[19]
Tobacco	[20]

Cadmium is ordinarily separated from modern wastewater by procedure ion exchange, ultra-filtration, RO, chemical precipitation, dissolvable extraction and other electrochemical treatments yet the techniques have a few impediments like high operational cost, delayed executional period, inadequate metal expulsion and production of large amount of toxic sludge that hard for disposal, which disallow their broad applications [12]. Adsorption utilizing ease materials as bio adsorbent is developing as a potential option in contrast to the current ordinary innovations for sequestration of heavy metal ions from aqueous solutions since this technique has numerous points of interest, for example, ease, high effectiveness, sludge minimal, simple recovery of adsorbents and probability of metal recuperation [21]. The search for new technologies able to remove metals from wastewaters has become a major topic for research. Different adsorbents that have been used for the removal of cadmium are given in Table 1.

Regarding the adsorbent used for the study, Leucaena *Leucocephala* is a leguminous tree that grows in the Mediterranean ecological conditions [22]. Young trees can reach a maximum height of more than 6 m in just two to three years period. [23]. Moreover, Leucaena *Leucocephala* is considered as a biomass with lignocellulosic content and it is a highly heterogeneous material. The presence of cellulose, hemicellulose and lignin in various proportions and structures is in charge of the variety among biomass species as far as their physical and chemical characteristics [2]. An advantages characteristic of Leucaena is high biomass production, capability to grow in nutrient poor soil, and high holocellulose content with low lignin [24]. Chemical properties of the Leucaena Leucocephala have functional groups such as hydroxyls, carboxyl's and carbonyl generates the main active binding sites for the adsorption of Cd (II) ions [25].

The aim of present study is to evaluate the functionality of Leucaena *Leucocephala* as bio sorbent to adsorb Cd (II) ions from aqueous solution. The effect of pH, adsorbent dosage and contact time for adsorption were studied.

II. MATERIALS AND METHODS

2.1. Chemicals and Adsorbent Preparations

A 1000 mg/l of Cd (II) ion stock solution was ready by dissolving a considerate amount of analytical grade reagent Cadmium Nitrate Tetrahydrate, $Cd (NO_3)_2.4H_2O$ in deionised water applying in a 1000 ml volumetric flask. Leucaena *Leucocephala* pods were collected at sample at Section 7, Shah Alam, Selangor. The samples were repeatedly washed with distilled water to remove unwanted particles and oven dried at 100^oC for 72 hours. The dried sample were cut into small pieces to remove the seeds. Then, the samples were grinded using a domestic grinder into a powder form and sieved to size of 300 µm using a normalized sieve. All the samples were then kept inside an airtight container for further use without any pre-treatment. The samples were labelled as the unmodified Leucaena Leucocephala (LL) and will be selected for Cd (II) ion sorption studies.

2.2. Pretreatment of Leucaena *Leucocephala* pods

2.2.1. Removal of Chlorophyll

200 mL of distilled water in the 250 mL beaker was boiled until it reached 100˚C. 100 g of dried Leucaena *Leucocephala* pods biomass of 400 μm was then placed into the beaker. The mixture was agitated at 220 rpm and at 290˚C for 10 minutes. It was filtered after cooling and the residue was dried in an oven overnight to a consistent weight at 105˚C. Next, 100 g of dried biomass that has been free of silica content was transferred into a 1000mL beaker. 500 mL of 96% ethanol was added. The mixture was stirred at 300 rpm at 60 ˚C for 3 hours. It was then filtered after cooling and the residue was dried in an oven until reached consistent weight at 105˚C [26].

2.2.2. Removal of Lignin

Silica free and Chlorophyll free of 100g of dried biomass were transferred into a 1000 mL and added with a 500 mL of 0.1 N HCl solution. The mixture was stirred for 3 hours at 50^oC with a magnetic stirrer. The residue was filtered and rinsed thoroughly with distilled water until neutral pH was achieved. It was oven dried at 80^oC for 48 hours until reached constant weight [27].

2.3. Adsorbent Characterization

2.3.1. Fourier Transform Infrared (FTIR) Spectroscopy

Fourier Transform Infrared (FTIR) Spectroscopy tests the vibrational properties of amino acids and cofactors, which are touchy to minute basic changes. The capacity of FTIR spectroscopy ready to choose shifted vibrations comparing to single concoction utilitarian gatherings engaged with an explicit response [28]. The Leucaena Leucocephala samples, before and after biosorption of heavy metals experiments were recorded by using Perkin Elmer Spectrum One FT-IR Spectrometer in the region of 4000 – 500 cm^{-1}. It was used to determine the different chemical functional groups present in the Leucaena *Leucocephala* and to determine the functional groups which are important for the metal binding with the Leucaena Leucocephala.

2.3.2. Thermo Gravimetric Analysis (TGA)

Thermo Gravimetric Analysis (TGA) is one of lab techniques in analytical chemistry for determining the characteristics of a substance through a change in percent of mass. It is to determine thermal stability, to predict the composition of materials and can characterize the weight loss due to decomposition, oxidation, reduction and also sorption or desorption by observing its weight reduction as a component of temperature amid warming procedure of the biomass [29]. The analysis was done using nitrogen gas at a heating rate of 10^oC per minute from 0^oC - 1000^oC by using Mettler-Toledo (M) TGA851/1600.

2.3.3. Inductively Coupled Plasma (ICP)

ICP-OES is one method of optical emission spectrometry. The sample solution is introduced into the system with high pressure which is produced by pumps into a nebulizer. where the sample is converted into an aerosol. A spray chamber is between nebulizer and torch which drains the excess droplets in aerosol through drain and allows the sample to pass into torch. In the torch, the atom components were excited during the sample analysis from outside when injected the plasma energy. Once the excited atoms come to low energy position, emission rays are discharged and the emission rays that correspond to the photon wavelength is collected by using various optics and wavelength devices are measured by using various detectors. The element type is determined based on the position of the photon rays, and the content of each element is determined based on the ray's intensity [30].

2.3.4. X-Ray Fluorescence (XRF)

X-ray fluorescence spectroscopy was also used by using Thermo-Fisher Scientific (Flash 2000 CHNS/O) Analyzer to identify the inorganic compound in the Leucaena *Leucocephala* pods as bio sorbent. Samples were pelletized to 6 mm masks using wax as binder with a powder to wax ratio of 10g to 3g and analyzed to identify the heavy metal ions in Leucaena *Leucocephala* pods bio sorbent [19].

2.4. Biosorption Experiment

Comprehensive investigation was conducted in this study for the bio sorbent with different parameters such as at different pH values (pH 2, pH 4, pH 6, pH 8, pH 10 and pH 12), bio sorbent dosage (0.05g, 0.25g, 0.50g, 0.75g and 1.0 g) and contact time (10, 20, 40, 60, 80, 100, 120, 140, 160 and 180 minutes) respectively. All the biosorption experiments were performed in triplicates and the data were recorded as average. Batch experiment were conducted to identify the efficiency of removing the Cd (II) ions from LL pods. It was carried out in a 250 mL conical flask filled with 100 mL of Cd (II) ion solution on a rotary shaker with 150 rpm. After a time period, the samples were filtered and collected into sample bottles to analyze the remaining metal ion concentration by using X-Ray Fluorescence (XRF) and Inductively Coupled Plasma (ICP) for the biosorption experiment [31].

III. RESULTS AND DISCUSSIONS

3.1. Characterization

3.1.1. FTIR

The FTIR spectrum were used to characterize the bio sorbent which it is a qualitative analysis to categorizes varying important functional groups for adsorption process such as carboxyl and hydroxyl [12]. The FTIR spectrum of Leucaena *Leucocephala* pods is shown in Fig. 1. As shown in Fig. 1, the spectra revealed a variety of adsorption peak and by comparison with the wavenumbers of raw Leucaena *Leucocephala* pods (1), modified Leucaena *Leucocephala* pods (2) and Leucaena *Leucocephala* pods after Cd (II) adsorption (3) there are significant changes occurred whereby some peaks were weakened or enhanced [14].

According to [11], the intense heavy metal ions adsorption peak occurs where the stretching vibrations at 3281 cm^{-1} depicted the presence hydroxyl groups on the surface of the Leucaena *Leucocephala* pods. The peak shifted to 3335 cm^{-1} for modified and to 3312 cm^{-1} for after Cd (II) ions adsorption indicates that the interactions with metal ions [32]. The raw bio sorbent shows a noticeable peak at 2918 cm^{-1} whereby it shows the asymmetric vibration of -CH whereas the stretching vibrations at peak 2850 cm^{-1} is because of CH_3-O [33]. The emergence peak in between region of 2918 cm^{-1} and 2925 cm^{-1} of the bio sorbent before and after adsorption can be explained as occurrence of the C–H stretching vibrations of aliphatic acids [11].

The peak shown at 1730 cm^{-1} may corresponds to the stretching vibrations of carboxylic double bond, C=O due to the non-ionic carboxyl groups whereby the asymmetric stretching vibration of ionic carboxylate groups appears at 1609 cm^{-1} and shifted to 1603 cm^{-1} is indicating strong adsorption peak [11]. The only peak shown at 1232 cm^{-1} may due to the stretching vibration of C-OH with ethanol [14]. From the peaks observed, the presence of lignin was significantly reduce where at the region peaks of 1500–1650 cm^{-1} shows the vibration of aromatic bonds C=C what can indicate the presence of lignin [34].

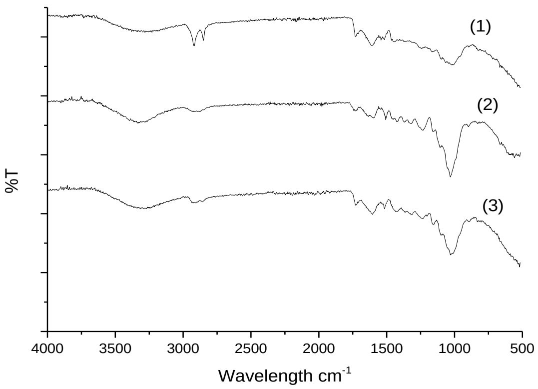

Figure 1: FTIR spectra of raw LL pods (1), modified LL pods (2) and LL after Cd (II) ions adsorption (3).

3.1.2. TGA

Referring to Fig 2., the Thermogravimetric Analysis (TGA) and the Differential Thermal Analysis (DTA) of precursor material were done in a thermogravimetric analyzer to verify the thermal stability and degradation of lignin in both raw and modified Leucaena *Leucocephala* pods and for both precursors show two different stages of weight loss [35]. Based on Fig. 2 (a)(ii) and (b)(ii), it indicates the amount of characteristics loss in weight was observed at two different stages during thermal decomposition where it corresponds to the weight loss of the sample upon continuous heating to 1000°C.

At the first stage for both precursors shows in the region between 0-60°C corresponds to rapid loss of about 5% of the sample weight due to loss of moisture content on the bio sorbent [36]. According to [37], it also described that the water vaporized at the initial weight loss below 100°C because of the hydrophilic features of the lignocellulosic bio sorbent. The second stage occurs at a derivative TG (DTG) peak of at 326°C and 367°C for raw and modified respectively. The temperature shifted at higher temperatures indicates that higher activation energy needed to decompose the bio sorbent which can associated to a higher content of cellulose and hemicellulose [35].

Both precursors show the decomposition process occurred in two stages. The first stage was found between 140-550°C whereby it was attributed to the decomposition of hemicellulose and cellulose, which can overlap at these temperatures [38]. The complex structure of lignin occurs degradation at the second stage of thermal decomposition and occurred in a wide range of temperatures weight loss at 512–1000°C about 53.66% with a residue weight of 10.73 mg at 1000°C found in the raw precursor but it shows a decrease of lignin content in the modified precursor whereby about 32.76% with a remainder weight of 6.55 mg at 1000°C [39]. Therefore, it can be observed that the lignocellulosic material in the bio sorbent is important which provide as active sites for adsorption because of low surface area and wide pore sizes properties are associated with liquid phase sorption for wastewater [19].

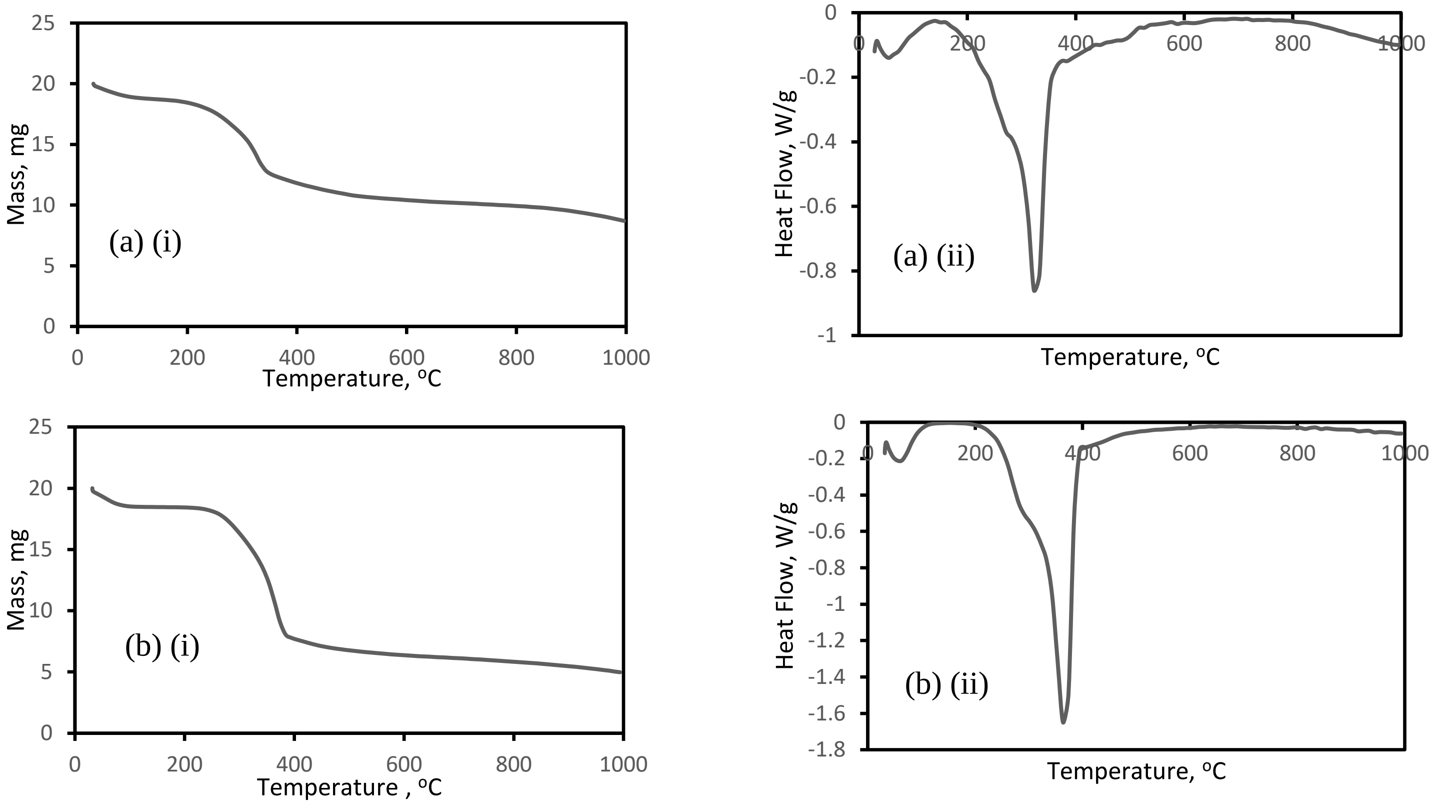

Figure 2: Thermogravimetric analysis (i) and DTG curve (ii) of raw Leucaena *Leucocephala* pods, (a) (i) (ii) and modified Leucaena *Leucocephala* pods (b) (i) (ii).

3.2. Effect on pH

The pH of an aqueous solution is an important parameter that affect the sorption of metal ions due to its effect on the specification of ions in the solution. According to [40], the bio sorbents surface has a variety of functional groups, such as carboxyl and hydroxyl groups, which have different affinity and specificity for metal binding. These groups are involved in almost all potential binding mechanisms. Moreover, the affinity of ionic species toward the functional groups present in the cellular surface is strongly affected by the pH value, in same as these functional groups to facilitate their removal by the adsorbents [19].

Surface charge is also an important subject that influences the sorption method and mechanism. The selected type of adsorbate for the adsorbent is important as it is depending on the pH as it affects the sorption mechanism, particularly for heavy metal ions because it changes the type of ionic species available and their degree of ionization within the adsorbate and the net charges on the surface of the adsorbent [41].

The indication for pH_{pzc} of Leucaena *Leucocephala* pods, the ($pH_{final} - pH_{initial}$) values were plotted against its corresponding initial pH (Fig. 3). From the data plotted, pH_{pzc} for Leucaena *Leucocephala* is at pH 6. The net surface charge of the adsorbent will stay as positive charge for any pH below pH_{pzc} and vice versa. Therefore, the results indicated that the Leucaena *Leucocephala* have acidic surface charges since the pH_{pzc} value is less than pH 7 [42]. Experimentally, Cd (II) solution at pH 2-12 were prepared respectively and the data obtained is shown in Fig. 4. Therefore, it can be signifying as the Leucaena *Leucocephala* pods were positively charged above pH 6 and negatively charged below pH 6.

From Fig. 4, the low percentage removal of Cd (II) ions depicted at pH 2 (adsorption capacity, 15.18%) are induced under these conditions occurred because of the sufficient energy provided onto the chemical reaction to overcome the repulsive forces instead of electrostatic reaction between the positively charged LL surface and the metal ion [43]. At pH 4 (adsorption capacity, 83.74%), there are large percentage removal of Cd (II) ions is resulted by electrostatic repulsion between both positively charged LL pods and Cd (II) ions when pH is lower than pH 6 (adsorption capacity, 79.28%) whereas at pH 8 (adsorption capacity, 83.58%), is attributed to the electrostatic attraction between different charges of LL pods (-) and Cd (II) ions (+) when pH is greater than 6.

However, according to [41], a declining percentage removal occurred at pH 6, resulting of $Cd(OH)^+$ throughout the pH adjustment process, it is because of the aggressive sorption between the positively charged metal cations (Cd^{2+} and $Cd(OH)^+$) with the negatively charged LL adsorbent.

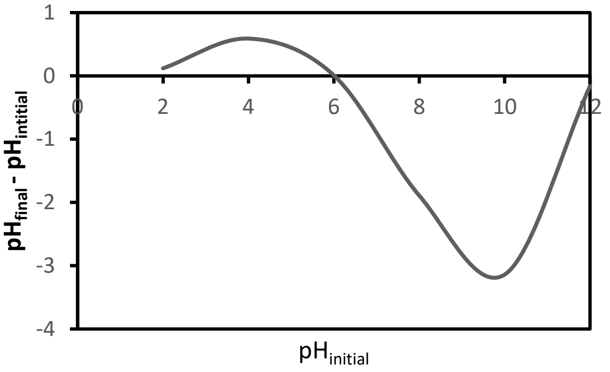

Figure 3: Percentage of Cd (II) ions adsorbed with varying pH for LL (agitation speed = 200 rpm; temperature = 27ºC; concentration = 50 mg/L).

In addition, the studied pH was up until pH 12. From pH 10-12, the percentage removal of Cd (II) ions gradually decreases as metal ion precipitation occurs due to the $Cd(OH)^+$ is further decompose by reaction with water to metal hydroxide, $Cd(OH)_2$, which forms a clump [7]. The principal species distributions of varied hydrolyzed Cd (II) ions are within the order of the subsequent reaction in equation (1) and (2) below:

$$Cd^{2+} + H_2O \leftrightarrow Cd(OH)^+ + H^+, \qquad pH=8 \qquad (1)$$

$$Cd(OH)^+ + H_2O \leftrightarrow Cd(OH)_2 + H^+, \qquad pH=12 \qquad (2)$$

Therefore, from Fig. 4, it can deduce as at low pH, there were many H^+ in the solution, which could compete with Cd (II) ions for sorption on the surface area. The adsorbed H^+ may reduce the quantity of negative charges on the surface of adsorbent. Whereas the pH increases, the quantity of H^+ in the solution reduced and the adsorption competition slowed subsequently. The more negative charges on the surface, the better adsorption of Cd (II) ions would be desirable [6].

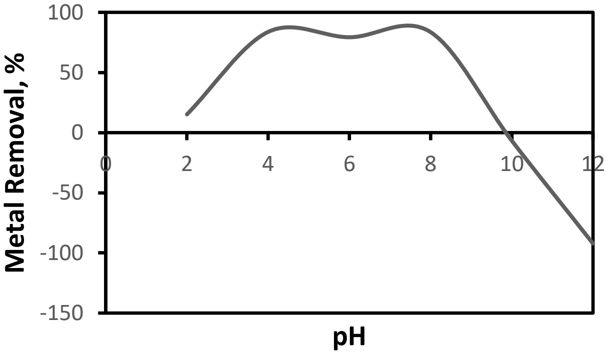

Figure 4: Effect of pH on removal of Cd (II) ions (C_0 = 50 mg/L; contact time = 20 min; agitation speed = 100 rpm; temperature = 25 °C)

3.3. Effect on Adsorbent Dosage

Data obtained from the experiments with varying adsorbent dosages are presented in Fig. 5 and Table 2. The Cd (II) ions concentration on the adsorbent surface increases significantly from 0.32% to 1.39% whereas the solution containing Cd (II) ions were gradually increases the percentage of adsorption from 64.39% to 96% (Fig. 5) as the amount of dosage increases from 0.05 g to 0.25 g. The data demonstrated that this phenomenon happened due to availability for the heavy metal ions to bind with the increasing active sites as the adsorbent dosage increases. Resulting the Cd (II) ions in the solution correlates with the many available surface of LL adsorbent [5].

However, the Cd (II) ions concentrations on the adsorbent surface decreases from 1.39% to 0.44% as the LL dosage increases from 0.25g to 1.0g whereas the solution containing Cd (II) ions were greatly increases the percentage of adsorption from 86.3% to 96% (Fig. 5). The decrease in efficiency at higher adsorbent dosage occurs because the aggregation of the particle interaction that led to the surface area reduction of the adsorbent [44] and more sorption sites on surface of the increasing LL dosage could not be saturated when the total Cd (II) ions concentration in solution was fixed [15].

The finding revealed that stage of equilibrium was met at the percentage of 95.2% at the dosage of 0.75g and cadmium percentage of 1.09. In addition, above than 0.75g, the sites for adsorption on the LL surface is not active. Therefore, the highest cadmium percentage was at 0.25g thus, the optimum dosage for Cd (II) ions adsorption.

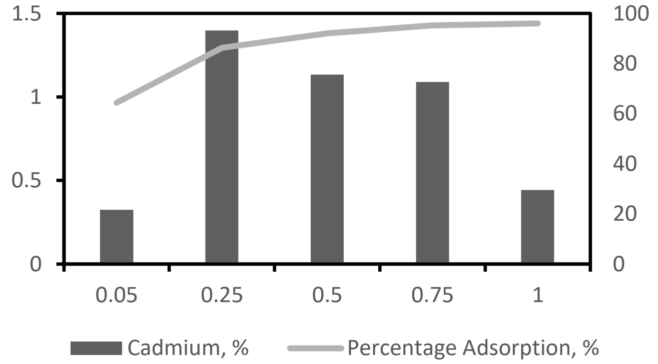

Figure 5: Effect on adsorbent dosage on removal of Cd (II) ions by LL (C_0 = 50 mg/L; agitation speed = 120 rpm; contact time = 24 hr; temperature = 25ºC; pH = 8)

Table 2: Effect of adsorbent dosage respect to metal concentration and percentage adsorption.

Dosage, g	Cadmium, %	Adsorption, %
0.05	0.3248	64.39
0.25	1.3972	86.3
0.5	1.1338	92.02
0.75	1.0899	95.28
1	0.4435	96

3.4. Effect on Contact Time

The relationship between contact time and Cd (II) ions removal by adsorption of LL for 180 min is illustrated in Figure 6. Results denote that as time increases, the high Cd (II) ions removed and obtained the highest percentage of adsorption at 55.46%. However, the rate of percentage adsorption was rapid, but the rate of adsorption evaluated as achieved equilibrium as time gradually decreases.

This occurred within time of 160 min and 55.12% of the cadmium adsorption percentage. However, even after 160 min of contact time, there are an increase of adsorption percentage up to 55.46%, but the margin difference is small thus, considered achieved equilibrium. The represent data can be defined from the rapid sorption in the early stage as high vacancy of surface area for Cd (II) adsorption [4]. In addition, this happened also because of the pores at the adsorbent surface area are fully saturated with the Cd (II) ions at equilibrium stage and adsorption process becomes plateau. The surplus of available sites of the adsorbent surface compete with Cd (II) ions due to repulsive forces. Therefore, it is clearly indicated that as the number of empty adsorption sites decreases for the Cd (II) ions, the rate of adsorption also decreases as shown in Fig. 4 and Table 3 [45].

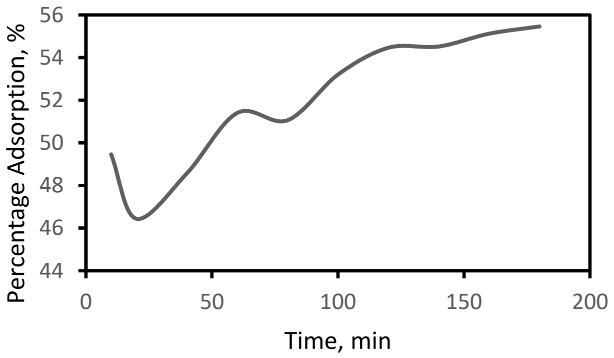

Figure 6: Effect on contact time on removal of Cd (II) ions by LL (C_0 = 50 mg/L; agitation speed = 120 rpm; contact time = 180 min; temperature = 25°C; pH = 4; adsorbent dosage = 0.50g)

Table 3: Effect on contact time respect to percentage adsorption.

Time, min	Percentage Adsorption, %
10	49.46
20	46.44
40	48.56
60	51.4
80	51.06
100	53.2
120	54.46
140	54.52
160	55.12
180	55.46

IV. CONCLUSION

From the present study, the significant data obtained shows that the modified Leucaena *Leucocephala* pods can be applied for the removal of Cd (II) with appropriate conditions largely depending on the pH, adsorbent dosage and contact time. Respectively, the maximum removal of Cd (II) ion on Leucaena *Leucocephala* pods is at pH 8, 0.25g of adsorbent dosage and a 160 min of contact time. As a conclusion, Leucaena Leucocephala pods are also a viable alternative of bio adsorbent for Cd (II) ions removal in wastewater water treatment.

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